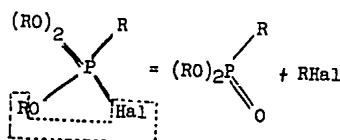




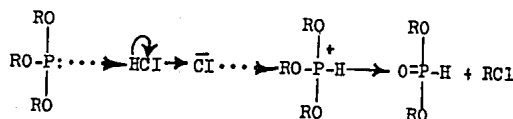
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Such a scheme of the Arbuzov rearrangement was confirmed by the preparation and isolation of the addition compound resulting from the interaction of methyl iodide with triphenylphosphite, as carried out by Michaelis and Kaehne [2], and by the decomposition of the addition compound into iodobenzene and the phenyl ester of methylphosphonic acid, as carried out by Arbuzov. This scheme is generally accepted and has been used as a guide in all the subsequent investigations of Arbuzov's school as well as of other chemists working in the field of organophosphorus compounds, although other examples of the formation of addition products from halogen derivatives and phosphites have not been obtained.

While studying the action of hydrogen chloride and acetyl chloride on phosphites prepared from optically active alcohols, Gerrard [3] discovered that the halogen derivatives thus formed possess a changed configuration, i.e., a Walden inversion takes place during the process. On this basis, he gives a complete and systematic explanation for the mechanism under consideration, especially in the dealkylation part of the process. The process is represented by the scheme



which indicates that the process may comprise two stages, and that the dealkylation is not intermolecular, but rather a process brought about by the approach of the anion, as a result of which the electron affinity of the oxygen atom will be increased by the positive charge [at P] so that a fission between alkyl and oxygen will be facilitated.

On the basis of studying reactions of isomeric ethoxypentenols and butenols with phosphorus trichloride, as a result of which isomeric ethoxychloropentenenes and chlorobutenes are formed, A. W. Pudovik draws a conclusion in regard to the mechanism of the Arbuzov rearrangement [4]. Pudovik, as well as Gerrard, assumes that the phosphites formed from the primary allyl alcohols react with a hydrogen ion of the hydrogen chloride that had split off, and that the reaction proceeds according to a bimolecular mechanism. In the case of secondary allyl alcohols, it proceeds almost completely according to a monomolecular mechanism with the intermediate formation of a carbonium ion. Further, Pudovik believes that this mechanism can be successfully used to explain the rearrangement of phosphites when they react with hydrogen chloride or alkyl halides. Under the circumstances, primary alkyl halides must react according to a bimolecular mechanism, secondary alkyl halides by a mixed mechanism, and tertiary halides exclusively by a monomolecular mechanism. These reasonings and conclusions are purely speculative and are based only on the proportions of isomeric ethoxychloropentenenes and chlorobutenes obtained by the author [Pudovik], and especially on the fact that no intermediate products were obtained with aliphatic phosphites.

Our investigations described in the present article involve a study of the reaction between  $\alpha, \beta$ -dibromodiethyl ether and aliphatic phosphites. These substances react at ordinary temperatures. That a reaction between  $\alpha, \beta$ -dibromodiethyl ethers and phosphites takes place is confirmed by the following

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evidence: (1) An evolution of heat felt by the hand takes place when the reagents are mixed together; in one experiment, when the temperature was measured, it was found to rise from  $-3$  to  $25^{\circ}$ ; (2) the disappearance, with time, of the odor characteristic for phosphites and of the sharp odor of  $\alpha,\beta$ -dibromodiethyl ether, which irritates the mucous membranes of the eyes and nose; (3) the change, with time, in the physical constants: the index of refraction decreases in a regular manner, while the specific gravity increases in a regular manner; judging by the changes in these constants, the reaction runs to completion at room temperature within 4-6 days; and (4) a decrease in volume when the reacting substances are combined, which continues until a constant volume is achieved.

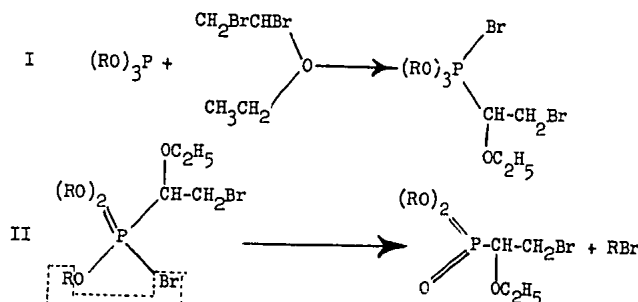
We obtained the addition products of  $\alpha,\beta$ -dibromodiethyl ether to aliphatic phosphites in the form of colorless, viscous liquids. We attempted to bring these liquids to a crystalline state by cooling them to a low temperature. The products we obtained did not crystallize on being cooled either in the free state or in solution, but assumed a solid, glasslike state. They were found to undergo a thermal decomposition analogous to the decomposition of the product resulting from addition of methyl iodide to triphenyl phosphite. As a result of the decomposition, we obtained the esters of  $\alpha$ -ethoxy- $\beta$ -bromoethylphosphonic acid.

As proof that, on heating, decomposition with the splitting off of alkyl halide actually takes place and not merely a distillation of alkyl halide already present in the mixture in a free state, we have the fact that a vacuum forms if the addition product is placed in a flask and connected to a vacuum, but not heated. However, if we heat the product to the temperature at which decomposition with the liberation of alkyl bromide begins, the vacuum is instantly broken.

We carried out experiments on the action of water on products of the addition of  $\alpha,\beta$ -dibromodiethyl ether to phosphites. From the reaction products we obtained esters of  $\alpha$ -ethoxy- $\beta$ -bromoethylphosphonic acid, whose constants are identical with the constants of esters prepared by thermal decomposition.

In this manner we carried out the interaction of  $\alpha,\beta$ -dibromodiethyl ether with aliphatic phosphites, which in accordance with the mechanism proposed by A. Ye. Arbuzov, takes place in two different, independent phases by the following scheme.

In the first phase, the reaction undoubtedly proceeds by a bimolecular mechanism. In the second phase, either intramolecular decomposition takes place,

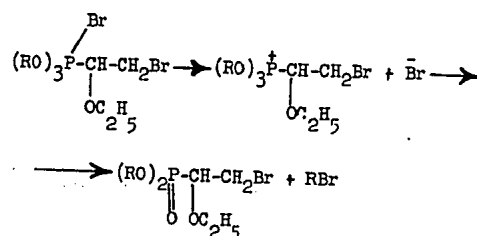


or ionization of the addition product occurs followed by a splitting off of alkyl halide by a bimolecular mechanism.

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We established qualitatively that aliphatic phosphites also react with monohalogen ethers and with esters of  $\alpha$ -halogeno-substituted carboxylic acids.

Therefore, the established mechanism for the rearrangement of phosphorus compounds is applicable to many reactions.

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Table 1. Phosphonic Acid Esters

Formula	Boiling Point (°C)	Pressure (mm)	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	MR		Phosphorus, (%)		Yield (%)
					Calculated	Found	Calculated	Found	
$\begin{array}{c} (\text{CH}_3\text{O})_2\text{P}-\text{CH}-\text{CH}_2\text{Br} \\ \parallel \\ \text{O} \quad \text{OC}_2\text{H}_5 \end{array}$	137-138	13	1.4648	1.4402	49.68	50.08	11.87	11.51; 11.70	64.4
$\begin{array}{c} (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{CH}-\text{CH}_2\text{Br} \\ \parallel \\ \text{O} \quad \text{OC}_2\text{H}_5 \end{array}$	140-140.5	9.5-9	1.4570	1.3180	58.91	59.73	10.72	10.53; 10.40	74.1
$\begin{array}{c} \text{n}(\text{C}_4\text{H}_9\text{O})_2\text{P}-\text{CH}-\text{CH}_2\text{Br} \\ \parallel \\ \text{O} \quad \text{OC}_2\text{H}_5 \end{array}$	176-178	13-12	1.4548	1.1909	77.38	78.61	8.98	9.00 8.99	52.3
$\begin{array}{c} \text{iso}(\text{C}_4\text{H}_9\text{O})_2\text{P}-\text{CH}-\text{CH}_2\text{Br} \\ \parallel \\ \text{O} \quad \text{OC}_2\text{H}_5 \end{array}$	170-171	14.5-14	1.4523	1.1839	77.38	78.66	8.98	9.19 8.90	53.2
$\begin{array}{c} (\text{C}_6\text{H}_5\text{O})_2\text{P}-\text{CH}-\text{CH}_2\text{Br} \\ \parallel \\ \text{O} \quad \text{OC}_2\text{H}_5 \end{array}$	Melting point 40-42	--	--	--	--	--	8.05	8.45; 8.30	--

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Table 2. Addition Products

Formula of Addition Product	Temper- ature of Bath (°C)	Physical Constants of Alkyl Halide						Yield (%)
		Boiling Point (°C)		$n_D^{20}$		$d_4^{20}$		
		Found	Literature	Found	Literature	Found	Literature	
$\begin{array}{c} \text{Br} \\   \\ (\text{CH}_3\text{O})_3\text{P}-\text{CH}-\text{CH}_2\text{Br} \\   \\ \text{OC}_2\text{H}_5 \end{array}$	60-65	--	--	--	--	--	--	85.1
$\begin{array}{c} \text{Br} \\   \\ (\text{C}_2\text{H}_5\text{O})_3\text{P}-\text{CH}-\text{CH}_2\text{Br} \\   \\ \text{OC}_2\text{H}_5 \end{array}$	60-80	38	38.2	1.4222	1.4239	1.4302	1.4300	85.4
$\begin{array}{c} \text{Br} \\   \\ n(\text{C}_4\text{H}_9\text{O})_3\text{P}-\text{CH}-\text{CH}_2\text{Br} \\   \\ \text{OC}_2\text{H}_5 \end{array}$	130-150	102	101.6	1.4402	1.4398	1.2768	1.2750	81.9
$\begin{array}{c} \text{Br} \\   \\ \text{iso}(\text{C}_4\text{H}_9\text{O})_3\text{P}-\text{CH}-\text{CH}_2\text{Br} \\   \\ \text{OC}_2\text{H}_5 \end{array}$	130-140	92-93	91.5	1.4352	1.4360	1.2632	1.2648	82.3

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